

B36

(19) World Intellectual Property Organization  
International Bureau



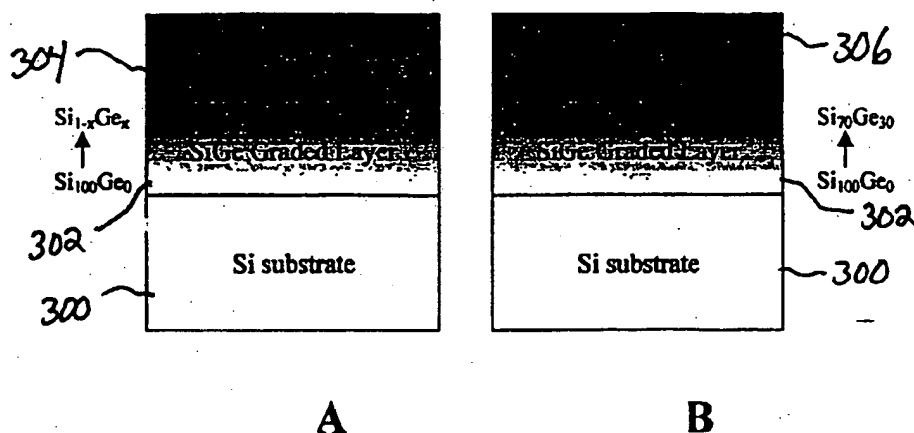
(43) International Publication Date  
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number  
WO 01/22482 A1

- (51) International Patent Classification<sup>7</sup>: H01L 21/20 (74) Agents: CONNORS, Matthew E. et al.; Samuels, Gauthier & Stevens LLP, 225 Franklin Street, Suite 3300, Boston, MA 02110 (US).
- (21) International Application Number: PCT/US00/40938
- (22) International Filing Date: 19 September 2000 (19.09.2000) (81) Designated States (national): CA, JP.
- (25) Filing Language: English (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- (26) Publication Language: English
- (30) Priority Data: 60/154,851 20 September 1999 (20.09.1999) US Published:  
— With international search report.  
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- (71) Applicant: AMBERWAVE SYSTEMS CORPORATION [US/US]; 165 New Boston Road, Woburn, MA 01801 (US).
- (72) Inventor: FITZGERALD, Eugene, A.; 7 Camelot Road, Windham, NH 02652 (US).
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF PRODUCING RELAXED SILICON GERMANIUM LAYERS



(57) Abstract: A method for making a semiconductor material, and subsequent structure, including providing a monocrystalline silicon substrate; epitaxially growing, using a source gas of Ge<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> for the germanium component, on the silicon substrate at a temperature in excess of 850 °C a graded Si<sub>1-x</sub>Ge<sub>x</sub> layer with increasing germanium concentration at a gradient of less than 25 % Ge per micron to a final composition in the range of 0.1 ≤ x ≤ 1; and epitaxially growing a layer of semiconductor material on the graded layer.

WO 01/22482 A1

**METHOD OF PRODUCING RELAXED SILICON GERMANIUM LAYERS****PRIORITY INFORMATION**

This application claims priority from provisional application Ser. No. 60/154,851 filed September 20, 1999.

5

**BACKGROUND OF THE INVENTION**

The invention relates to the field of relaxed SiGe layers.

The application of relaxed SiGe layers on Si substrates in optoelectronics and electronics demands that an economical method of forming high quality material be  
10 obtained. A summary of the development of relaxed SiGe materials and their application can be found in "Silicon-based Microphotonics and Integrated Optoelectronics", by E.A. Fitzgerald and L.C. Kimerling, MRS Bulletin vol. 23 (1998). Additional details to their specific application in SiGe/Si heterostructures can be found in "SiGe Nanostructures", E.A. Fitzgerald, Annual Review of Material Science p. 417 (1995). In these references, the  
15 relaxed SiGe buffers are deposited via chemical vapor deposition (CVD).

CVD is, under most conditions and products, the most economical method of depositing thin layers of crystalline semiconductors. High thin-film growth rates are essential in producing economical relaxed SiGe materials on Si substrates, since the SiGe layers are relatively thick. The highest growth rates known to date, which have been  
20 deposited in non-commercial equipment, have been achieved with CVD, with a maximum growth rate of about 6 micrometers per hour.

Current methods of producing SiGe relaxed buffers in research environments consist of using, typically, silane or dichlorosilane for the silicon source gas, and germane for the germanium source gas. The silane molecule is a silicon atom surrounded by 4 hydrogen  
25 atoms, the dichlorosilane is the same except 2 of the hydrogen atom are replaced with chlorine atoms, and germane is a germanium atom bonded to 4 hydrogen atoms. These gases are flowed across a hot Si wafer. The gases breakdown and deposit the Si or Ge atom on the semiconductor substrate, and if the substrate is at a sufficient temperature, crystalline thin film growth proceeds.

30 An upper limit in the thin film growth rate is defined by two main factors. One factor is that the CVD deposition equipment can become too coated with thin film deposit in areas other than the substrate area. If this deposition is too great, it may prevent a large number of consecutive wafer deposition processes, leading to greater cost. An additional

problem is that in attempting to deposit films at high growth rates, gas-phase nucleation can occur, in which particles of SiGe, Si, or Ge form in the gas stream and subsequently deposit on the wafer surface.

This incorporation of particles into the epitaxial film not only degrades the material quality locally, but also serves as heterogeneous nucleation sites for additional threading dislocations. As a result, high temperature, high growth rate depositions result in material with high defect concentrations and poor surface morphology. Thus, in the conventional gas chemistry used for CVD deposition, there is a problem producing the highest quality films at high growth rates.

The origin of this problem is the decomposition temperature of germane. The germane molecule decomposes at an even lower temperature than silane. Therefore, for a given temperature and gas concentration, there will be increased levels of gas phase nucleation and equipment coating when germane is used. This problem is exacerbated for high concentration germanium films, because the germanium concentration in the gas phase is proportionately higher. Since many of the applications for relaxed SiGe require Ge concentrations greater than 10%, these problems are quite severe for the majority of relaxed SiGe thin film growths.

### SUMMARY OF THE INVENTION

One solution to the problems of the prior art is to change the gas chemistry such that equipment coating and gas phase nucleation of particles is reduced. It is therefore desirable to use a germanium source that decomposes at a higher temperature.

Accordingly, the invention provides a method for making a semiconductor material, and subsequent structure, including providing a monocrystalline silicon substrate; epitaxially growing, using a source gas of  $\text{Ge}_x\text{H}_y\text{Cl}_z$  for the germanium component, on the silicon substrate at a temperature in excess of  $850^\circ\text{C}$  a graded  $\text{Si}_{1-x}\text{Ge}_x$  layer with increasing germanium concentration at a gradient of less than 25% Ge per micron to a final composition in the range of  $0.1 \leq x \leq 1$ ; and epitaxially growing a layer of semiconductor material on the graded layer.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the growth rate of epitaxial silicon as a function of growth temperature for a variety of Si source gases;

FIG. 2 is a graph of the threading dislocation density at the surface of a relaxed SiGe graded layer versus growth temperature for a CVD reactor; and

FIGs. 3A and 3B are schematic block diagrams of exemplary structures with a uniform cap layer of  $\text{Si}_{1-x}\text{Ge}_x$  ( $0 < x \leq 1$ ) and  $\text{Si}_{0.7}\text{Ge}_{0.3}$ , respectively, on a silicon substrate  
5 using a relaxed SiGe graded buffer layer in accordance with the invention.

### **DETAILED DESCRIPTION OF THE INVENTION**

FIG. 1 is a graph showing the growth rate of silicon versus temperature for various source gases. Two distinct growth regimes are evident. For low temperatures, the growth rate has an exponential dependence on temperature, indicating that the growth is reaction  
10 rate or kinetically limited. For high temperatures, the growth rate has a weak dependence on temperature, indicating that the growth is mass transport or diffusion limited. Epitaxial layers are formed in the mass transport limited regime to minimize the effects of temperature variations during growth.

It is well known that as more hydrogen atoms in the silane molecule are replaced  
15 with chlorine atoms, the decomposition temperature of the source gas increases. This effect is evidenced by the shift of the reaction-limited regime to higher temperatures for source gases with increasing chlorine content. For example, the silicon tetrachloride ( $\text{SiCl}_4$ ) growth curve is shifted over  $200^\circ\text{C}$  toward higher temperatures from the silane ( $\text{SiH}_4$ ) growth curve. As a result, epitaxial films can be grown with  $\text{SiCl}_4$  at much higher temperatures than with  
20  $\text{SiH}_4$  without the effects of gas phase nucleation and equipment coating. Additionally, extremely high growth rates can be achieved at high temperatures using these chlorine-based source gas chemistries.

Since the main problem in SiGe film growth is the low decomposition temperature of the germane gas, our invention uses a germanium-chlorine-based gas to increase the  
25 decomposition temperature. As in the silicon system, chlorogermanes can be used to extend growth temperatures to more than  $200^\circ\text{C}$  over germane growth temperatures without increasing gas phase nucleation. In this way, the decomposition temperatures of the gases can be optimally chosen such that very high growth rates can be achieved at high temperatures. The most readily available germanium-chlorine source gas is germanium  
30 tetrachloride, ( $\text{GeCl}_4$ ). This gas, unlike germane, can be used at growth temperatures in excess of  $800^\circ\text{C}$  to grow thick, relaxed SiGe layers without excessive equipment coating and particle formation. It can be combined with any of the source gases for silicon, such as silane, dichlorosilane, trichlorosilane, and silicon tetrachloride to form high quality SiGe

layers.

The ability to deposit films at high temperatures using germanium tetrachloride also results in lower threading dislocation densities in the relaxed graded layer. The dislocation density in a relaxed graded structure is exponentially dependent on the temperature during growth. FIG. 2 is a graph showing experimental data of dislocation density versus growth temperature for SiGe graded layers. Currently, SiGe relaxed buffers with a 30% Ge final composition cannot be grown much above 800°C without experiencing severe gas phase nucleation.

Using conventional source gases at a growth temperature of 800°C results in a dislocation density in the mid- $10^5$  cm<sup>-2</sup> range. With the germanium tetrachloride process, this growth temperature can be extended to over 1000°C without particle deposits or equipment coating. From Figure 2, it is evident that growth temperatures equal to or greater than 1000°C result in films with dislocation densities in the sub- $10^5$  cm<sup>-2</sup> regime. Thus, by incorporating a different source gas for germanium introduction, the defect density in the relaxed SiGe layers is improved (lowered).

The structure that is deposited using this gas chemistry is similar to that outlined in Brasen et al., U.S. Pat. No. 5,221,413, incorporated herein by reference. FIGs. 3A and 3B are schematic block diagrams of exemplary structures with a uniform cap layer of Si<sub>1-x</sub>Ge<sub>x</sub> ( $0 < x \leq 1$ ) and Si<sub>0.7</sub>Ge<sub>0.3</sub>, respectively, on a silicon substrate using a relaxed SiGe graded buffer layer in accordance with the invention. The structures include a monocrystalline silicon substrate 300, a SiGe graded buffer layer 302, and a uniform concentration SiGe cap layer 304, 306. The SiGe buffer layer 302 is a series of SiGe layers with increasing Ge concentration, usually with a gradient of less than 25% Ge per micron. By increasing the Ge concentration gradually, the strain due to the lattice mismatch between Si and Ge is relieved and the threading dislocation density is minimized. The cap layers are high quality SiGe layer with uniform Ge concentration that can be used as a platform for device fabrication.

FIG. 3A shows a generic structure where the cap layer 304 Ge concentration can vary from  $0 < x \leq 1$ . FIG. 3B shows a structure where the cap layer 306 is Si<sub>0.7</sub>Ge<sub>0.3</sub>. By using the germanium-chlorine based source gases described herein, these structures can be constructed with fewer defects and at a lower cost.

Although the present invention has been shown and described with respect to several preferred embodiments thereof, various changes, omissions and additions to the

form and detail thereof, may be made therein, without departing from the spirit and scope of the invention.

What is claimed is:

CLAIMS

1        1. A method for making a semiconductor material comprising the steps of:  
2        providing a monocrystalline silicon substrate;  
3        epitaxially growing, using a source gas of  $\text{Ge}_x\text{H}_y\text{Cl}_z$  for the germanium component,  
4        on said silicon substrate at a temperature in excess of  $850^\circ\text{C}$  a graded  $\text{Si}_{1-x}\text{Ge}_x$  layer with  
5        increasing germanium concentration at a gradient of less than 25% Ge per micron to a final  
6        composition in the range of  $0.1 \leq x \leq 1$ ; and  
7        epitaxially growing a layer of semiconductor material on said graded layer.

1        2. The method in claim 1 further comprising the step of incorporating a source gas  
2        of  $\text{Ge}_x\text{H}_y\text{Cl}_z$  for the germanium component and silane gas for the silicon component.

1        3. The method in claim 1 further comprising the step of incorporating a source gas  
2        of  $\text{Ge}_x\text{H}_y\text{Cl}_z$  for the germanium component and dichlorosilane gas for the silicon component.

1        4. The method in claim 1 further comprising the step of incorporating a source gas  
2        of  $\text{Ge}_x\text{H}_y\text{Cl}_z$  for the germanium component and trichlorosilane gas for the silicon component.

1        5. The method in claim 2, wherein the source gas for the germanium component  
2        comprises germanium tetrachloride ( $\text{GeCl}_4$ ).

1        6. The method in claim 3, wherein the source gas for the germanium component  
2        comprises germanium tetrachloride ( $\text{GeCl}_4$ ).

1        7. The method in claim 4, wherein the source gas for the germanium component  
2        comprises germanium tetrachloride ( $\text{GeCl}_4$ ).

1        8. A semiconductor structure comprising:  
2        a monocrystalline silicon substrate;  
3        a graded  $\text{Si}_{1-x}\text{Ge}_x$  layer epitaxially grown, using a source gas of  $\text{Ge}_x\text{H}_y\text{Cl}_z$  for the  
4        germanium component, on said silicon substrate at a temperature in excess of  $850^\circ\text{C}$  with  
5        increasing germanium concentration at a gradient of less than 25% Ge per micron to a final

7

6 composition in the range of  $0.1 \leq x \leq 1$ ; and

7 a layer of semiconductor material epitaxially grown on said graded layer.



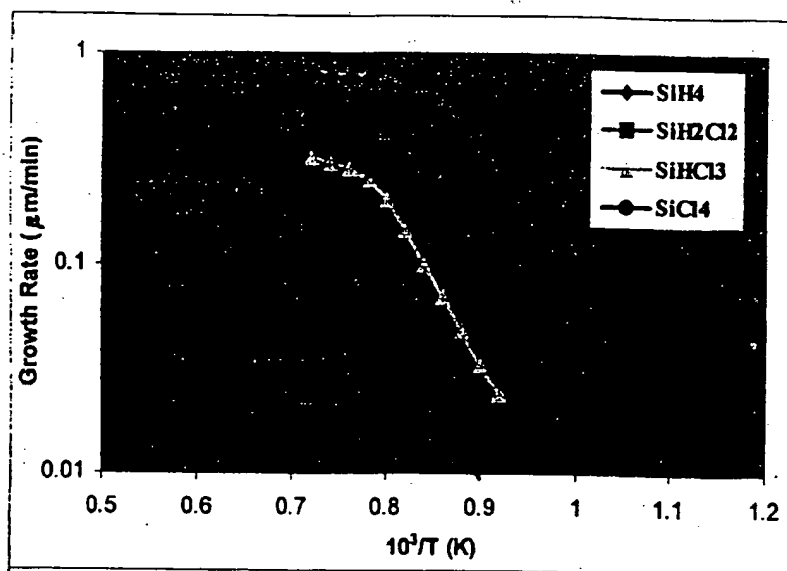
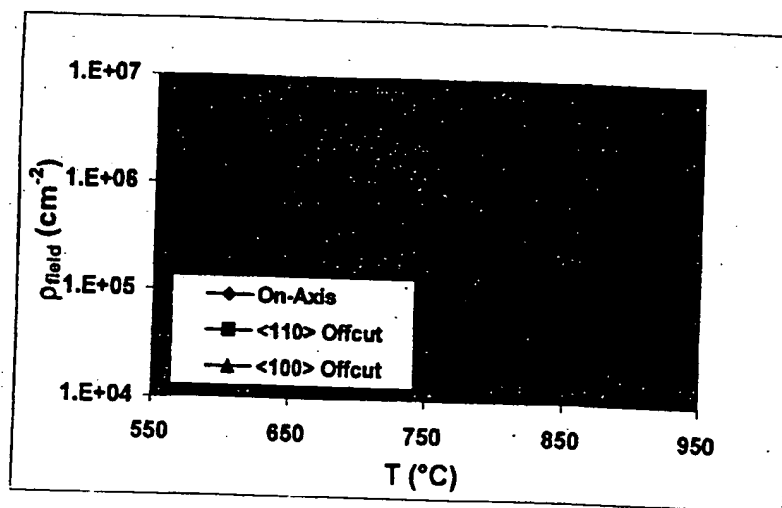


FIG. 1

**FIG. 2**

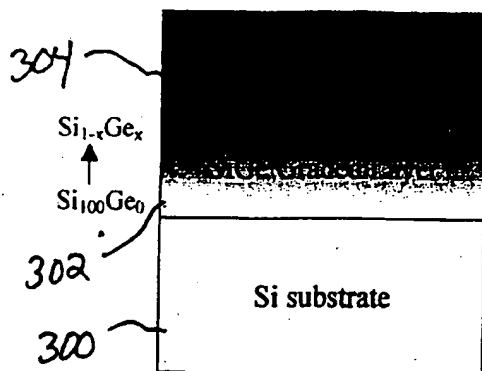


FIG. 3A

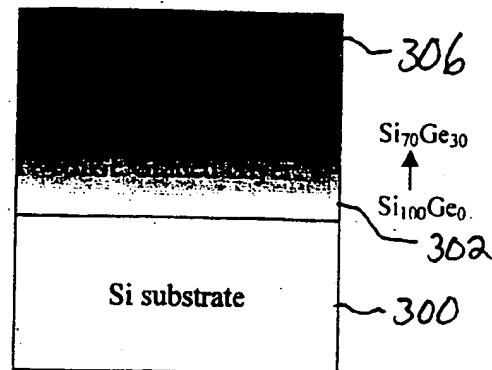


FIG. 3B

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/40938

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H01L21/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 935 040 A (MASON DONALD R) 27 January 1976 (1976-01-27) column 2, line 20 - column 3, line 22 ---	1,2,4,5, 7,8
X	EP 0 514 018 A (AMERICAN TELEPHONE & TELEGRAPH) 19 November 1992 (1992-11-19) cited in the application page 3, line 15 - line 45 example 2 -----	1,3,8

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*S\* document member of the same patent family

Date of the actual completion of the international search

23 February 2001

Date of mailing of the international search report

02/03/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Giordani, S

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/40938

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3935040 A	27-01-1976	US 3985590 A	12-10-1976
		US 3984857 A	05-10-1976
		US 3766447 A	16-10-1973
EP 0514018 A	19-11-1992	US 5221413 A	22-06-1993
		JP 2792785 B	03-09-1998
		JP 6252046 A	09-09-1994
		US 5442205 A	15-08-1995